

IN THE UNITED STATES PATENT AND TRADEMARK OFFICE

DECLARATION OF ACCURACY OF TRANSLATION

The undersigned translator, Sachiko Miki of TSUKUNI & ASSOCIATES having an office at 1-22-12, Toranomom, Minato-ku, Tokyo, Japan states that:

- (1) I am fully conversant both with the Japanese and English languages.
- (2) I have carefully compared the attached English-language translation of Japanese Patent Application Number 2002-286878, filed September 30, 2002 with the original Japanese-language patent application.
- (3) The translation is, to the best of my knowledge, and belief, an accurate translation from the original into the English language.

Date: April 8, 2008

S. Miki
Sachiko Miki

[Document name] Specification

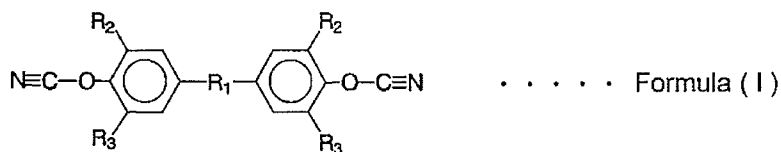
[Title of the invention] RESIN COMPOSITION FOR PRINTED WIRING BOARD AND VARNISH, PREPREG AND METAL CLAD LAMINATED BOARD USING THE SAME

[Scope of claim for patent]

[Claim 1] A resin composition for printed wiring board characterized in comprising (A) a cyanate ester compound having 2 or more cyanate groups in the molecule and/or a prepolymer thereof, (B) an epoxy resin containing at least one kind of an epoxy resin having a biphenyl structure in the molecule.

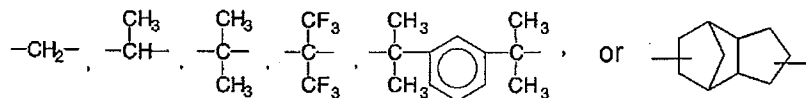
[Claim 2] The resin composition for printed wiring board according Claim 1, wherein Component (A) is at least one kind selected from the group consisting of a cyanate ester compound represented by the formula (I):

[Formula 1]



(wherein R₁ represents

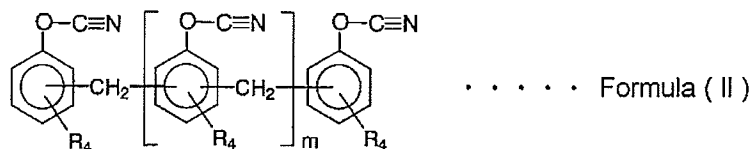
[Formula 2]



R₂ and R₃ each represent a hydrogen atom or an alkyl group having 1 to 4 carbon atoms, and each may be the same or different from each other)

and a cyanate ester compound represented by the formula (II):

[Formula 3]



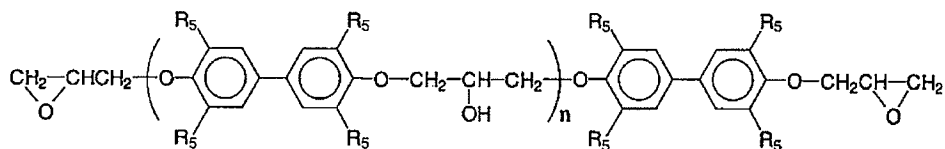
(wherein R_4 represents a hydrogen atom or an alkyl group having 1 to 4 carbon atoms, m represents an integer of 1 to 7)

and a prepolymer thereof.

[Claim 3] The resin composition for printed wiring board according to Claim 1 or 2, wherein Component (A) is at least one selected from the group consisting of 2,2-bis(4-cyanatophenyl)propane, bis(4-cyanatophenyl)ethane, bis(3,5-dimethyl-4-cyanatophenyl)methane, 2,2-bis(4-cyanatophenyl)-1,1,1,3,3,3-hexafluoropropane, α,α' -bis(4-cyanatophenyl)- m -diisopropylbenzene, a cyanate ester compound of a phenol-added dicyclopentadiene polymer, a phenol novolac type cyanate ester compound and a cresol novolac type cyanate ester compound and a prepolymer thereof.

[Claim 4] The resin composition for printed wiring board according to any one of Claims 1 to 3, wherein the epoxy resin having a biphenyl structure in the molecule in Component (B) is at least one selected from the group consisting of an epoxy resin represented by the formula (III):

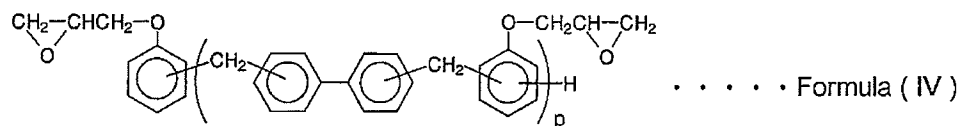
[Formula 4]



. Formula (III)

(wherein R_5 each represent a hydrogen atom or a methyl group, n represents an integer of 0 to 6) and an epoxy resin represented by the formula (IV):

[Formula 5]



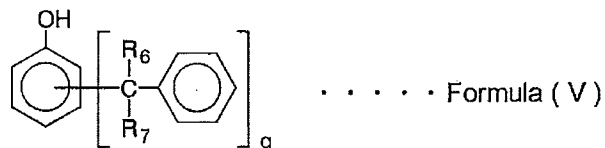
(wherein p represents an integer of 1 to 5.)

[Claim 5] The resin composition for printed wiring board according to any one of Claims 1 to 4, wherein Component (B) is contained in an amount of 10 to 250 parts by weight based on 100 parts by weight of Component (A).

[Claim 6] The resin composition for printed wiring board according to any one of Claims 1 to 5, which further comprises (C) a monovalent phenol compound.

[Claim 7] The resin composition for printed wiring board according to Claim 6, wherein Component (C) is represented by the formula (V):

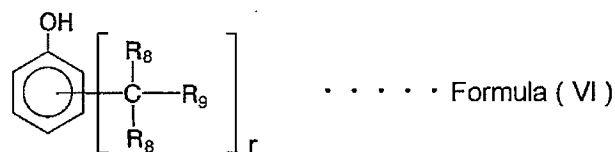
[Formula 6]



(wherein R₆ and R₇ each represent a hydrogen atom or a methyl group, each may be the same or different from each other, and q represents an integer of 1 to 3)

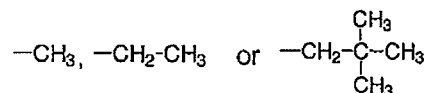
and a monovalent phenol compound represented by the formula (VI):

[Formula 7]



(wherein R₈ represents a hydrogen atom or a methyl group, R₉ represents

[Formula 8]



And r represents an integer of 1 or 2.)

[Claim 8] The resin composition for printed wiring board according to Claims 6 or 7, wherein Component (C) is at least one selected from the group consisting of p-(α -cumyl)phenol, mono-, di- or tri-(α -methylbenzyl)phenol, p-tert-butylphenol, 2,4- or 2,6-di-tert-butylphenol, p-tert-amylphenol and p-tert-octylphenol.

[Claim 9] The resin composition for printed wiring board according to any one of Claims 6 to 8, wherein Component (B) is contained in an amount of 10 to 250 parts by weight based on 100 parts by weight of Component (A), and Component (C) is contained in an amount of 2 to 60 parts by weight based on the same.

[Claim 10] A resin varnish for a printed wiring board obtained by dissolving or dispersing the resin composition for printed wiring board according to any one of Claims 1 to 9 in a solvent.

[Claim 11] A prepreg for a printed wiring board which is obtained by impregnating the resin composition for printed wiring board according to any one of Claims 1 to 9 or the resin varnish for a printed wiring board according to Claim 10 into a substrate, and drying at 80 to 200°C.

[Claim 12] A metal clad laminated board which is obtained by laminating one or more of the prepreg for a printed wiring board according to Claim 11, laminating a metal foil on at least one surface thereof and pressurizing under heating.

[Claim 13] A resin composition for printed wiring board characterized in comprising a phenol-modified cyanate ester oligomer obtainable by reacting (A) a cyanate ester compound having 2 or more cyanate groups in the molecule

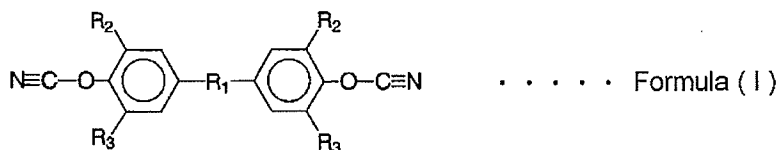
and/or a prepolymer thereof and (C) a monovalent phenol compound, and

(B) an epoxy resin containing at least one kind of an epoxy resin having a biphenyl structure in the molecule.

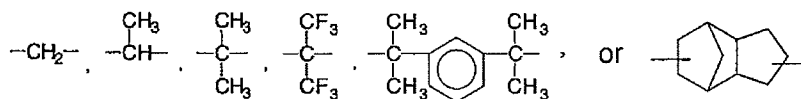
[Claim 14] The resin composition for printed wiring board according to Claim 13, which further comprises (C) a monovalent phenol compound.

[Claim 15] The resin composition for printed wiring board according to any one of Claims 13 or 14, wherein Component (A) is at least one selected from the group consisting of a cyanate ester compound represented by the formula (I):

[Formula 9]



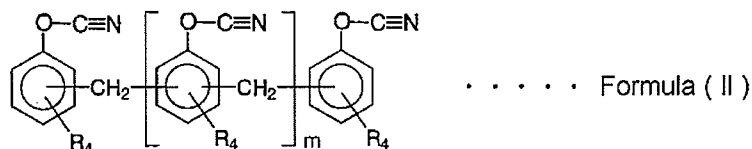
(wherein R_1 represents



R_2 and R_3 each represent a hydrogen atom or an alkyl group having 1 to 4 carbon atoms, and each may be the same or different from each other)

and a cyanate ester compound represented by the formula (II):

[Formula 11]



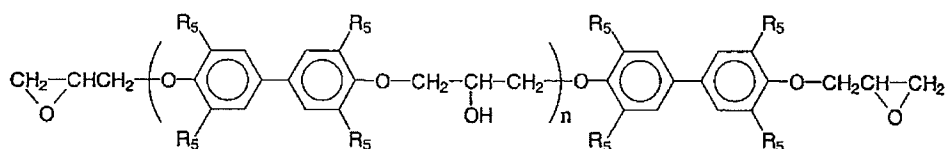
(wherein R_4 represents a hydrogen atom or an alkyl group having 1 to 4 carbon atoms, m represents an

integer of 1 to 7)
and a prepolymer thereof.

[Claim 16] The resin composition for printed wiring board according to any one of Claims 13 to 15, wherein Component (A) is at least one selected from the group consisting of 2,2-bis(4-cyanatophenyl)propane, bis(4-cyanatophenyl)ethane, bis(3,5-dimethyl-4-cyanatophenyl)methane, 2,2-bis(4-cyanatophenyl)-1,1,1,3,3,3-hexafluoropropane, α,α' -bis(4-cyanatophenyl)-m-diisopropylbenzene, a cyanate ester compound of a phenol-added dicyclopentadiene polymer, a phenol novolac type cyanate ester compound and a cresol novolac type cyanate ester compound and a prepolymer thereof.

[Claim 17] The resin composition for printed wiring board according to any one of Claims 13 to 16, wherein the epoxy resin having a biphenyl structure in the molecule in Component (B) is at least one selected from the group consisting of an epoxy resin represented by the formula (III):

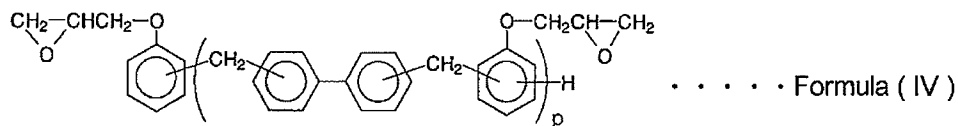
[Formula 12]



Formula (III)

(wherein R₅ each represent a hydrogen atom or a methyl group, n represents an integer of 0 to 6)
and an epoxy resin represented by the formula (IV):

[Formula 13]



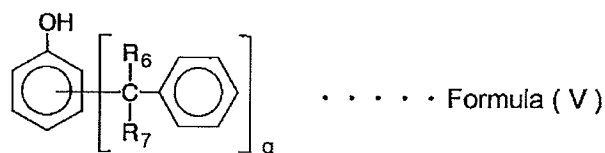
Formula (IV)

(wherein p represents an integer of 1 to 5.)

[Claim 18] The resin composition for printed wiring

board according to any one of Claims 13 to 17, wherein Component (C) is represented by the formula (V):

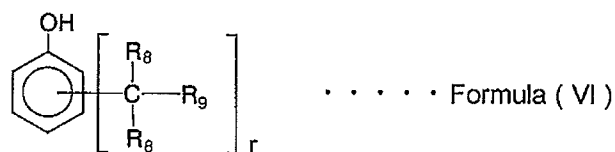
[Formula 14]



(wherein R_6 and R_7 each represent a hydrogen atom or a methyl group, each may be the same or different from each other, and q represents an integer of 1 to 3)

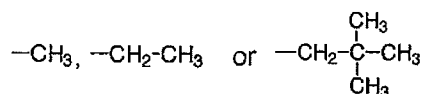
and a monovalent phenol compound represented by the formula (VI):

[Formula 15]



(wherein R_8 represents a hydrogen atom or a methyl group, R_9 represents

[Formula 16]



and r represents an integer of 1 or 2.)

[Claim 19] The resin composition for printed wiring board according to Claim 18, wherein Component (C) is at least one selected from the group consisting of p-(α -cumyl)phenol, mono-, di- or tri-(α -methylbenzyl)phenol, p-tert-butylphenol, 2,4- or 2,6-di-tert-butylphenol, p-tert-amylphenol and p-tert-octylphenol.

[Claim 20] The resin composition for printed wiring board according to any one of Claims 13 to 19, wherein the

phenol-modified cyanate ester oligomer is a phenol-modified cyanate ester oligomer obtainable by reacting 100 parts by weight of Component (A) and 60 parts by weight of Component (C), and Component (B) is contained in an amount of 10 to 250 parts based on the same.

[Claim 21] The resin composition for printed wiring board according to any one of Claims 13 to 19, wherein the phenol-modified cyanate ester oligomer is a phenol-modified cyanate ester oligomer obtainable by reacting 100 parts by weight of Component (A), 0.4 parts by weight or more and less than 60 parts by weight of Component (C), and Component (B) is contained in an amount of 10 to 250 parts by weight, and Component (C) is additionally contained in a total amount of 2 to 60 parts by weight which is the sum of the amount with Component (C) to be used for formation of the phenol-modified cyanate ester oligomer.

[Claim 22] A resin varnish for a printed wiring board obtainable by dissolving or dispersing the resin composition for printed wiring board according to any one of Claims 13 to 21.

[Claim 23] resin composition for printed wiring board A prepreg for a printed wiring board which is obtainable by impregnating the resin composition for printed wiring board according to any one of Claims 13 to 21 or the resin varnish for a printed wiring board according to Claim 22 into a substrate, and drying at 80 to 200°C..

[Claim 24] The metal clad laminated board which is obtainable by laminating one or more of the prepreg for a printed wiring board according to Claim 23, laminating a metal foil on at least one surface thereof and pressurizing under heating.

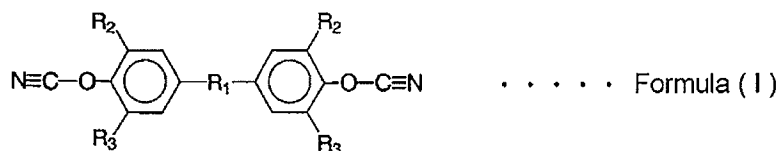
[Claim 25] The resin composition for printed wiring board characterized in comprising an epoxy/phenol-modified cyanate ester oligomer obtainable by reacting (A) a cyanate ester compound having 2 or more cyanate groups in the

molecule and/or a prepolymer thereof, (B) an epoxy resin containing at least one kind of an epoxy resin containing a biphenyl structure, and (C) a monovalent phenol compound.

[Claim 26] The resin composition for printed wiring board according to Claim 25, which further comprises (C) a monovalent phenol compound.

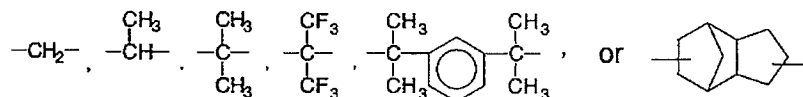
[Claim 27] The resin composition for printed wiring board according to any one of Claims 25 or 26, wherein Component (A) is at least one selected from the group consisting of a cyanate ester compound represented by the formula (I):

[Formula 17]



(wherein R₁ represents

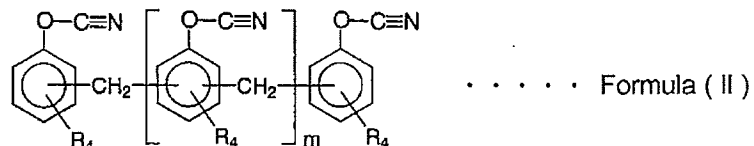
[Formula 18]



(R₂ and R₃ each represent a hydrogen atom or an alkyl group having 1 to 4 carbon atoms, and each may be the same or different from each other)

and a cyanate ester compound represented by the formula (II):

[Formula 19]



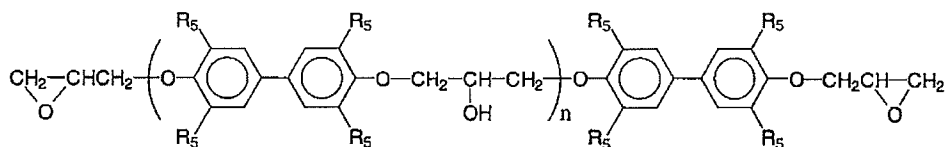
(wherein R₄ represents a hydrogen atom or an alkyl group having 1 to 4 carbon atoms, m represents an

integer of 1 to 7)
and a prepolymer thereof.

[Claim 28] The resin composition for printed wiring board according to any one of Claims 25 to 27, wherein Component (A) is at least one selected from the group consisting of 2,2-bis(4-cyanatophenyl)propane, bis(4-cyanatophenyl)ethane, bis(3,5-dimethyl-4-cyanatophenyl)methane, 2,2-bis(4-cyanatophenyl)-1,1,1,3,3,3-hexafluoropropane, α,α' -bis(4-cyanatophenyl)-m-diisopropylbenzene, a cyanate ester compound of a phenol-added dicyclopentadiene polymer, a phenol novolac type cyanate ester compound and a cresol novolac type cyanate ester compound and a prepolymer thereof.

[Claim 29] The resin composition for printed wiring board according to any one of Claims 25 to 28, wherein the epoxy resin having a biphenyl structure in the molecule in Component (B) is at least one selected from the group consisting of an epoxy resin represented by the formula (III):

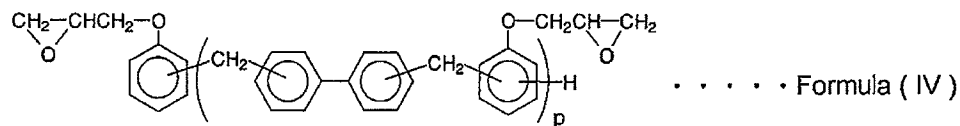
[Formula 20]



Formula (III)

(wherein R_5 each represent a hydrogen atom or a methyl group, n represents an integer of 0 to 6)
and an epoxy resin represented by the formula (IV):

[Formula 21]



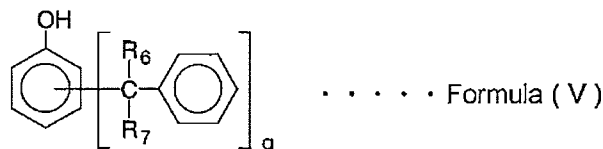
Formula (IV)

(wherein p represents an integer of 1 to 5.)

[Claim 30] The resin composition for printed wiring

board according to any one of Claims 25 to 29, wherein Component (C) is represented by the formula (V):

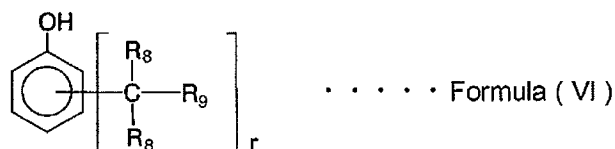
[Formula 22]



(wherein R_6 and R_7 each represent a hydrogen atom or a methyl group, each may be the same or different from each other, and q represents an integer of 1 to 3)

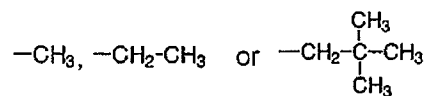
and a monovalent phenol compound represented by the formula (VI):

[Formula 23]



(wherein R_8 represents a hydrogen atom or a methyl group, R_9 represents

[Formula 24]



and r represents an integer of 1 or 2.)

[Claim 31] The resin composition for printed wiring board according to Claim 30, wherein Component (C) is at least one selected from the group consisting of p-(α -cumyl)phenol, mono-, di- or tri-(α -methylbenzyl)phenol, p-tert-butylphenol, 2,4- or 2,6-di-tert-butylphenol, p-tert-amylphenol and p-tert-octylphenol.

[Claim 32] The resin composition for printed wiring board according to Claim 25 to 31, wherein the

epoxy/phenol-modified cyanate ester oligomer is an epoxy/phenol-modified cyanate ester oligomer obtainable by reacting 100 parts by weight of Component (A), 10 to 250 parts by weight of Component (B), and 2 to 60 parts by weight of Component (C).

[Claim 33] The resin composition for printed wiring board according to any one of Claims 25 to 31, wherein the epoxy/phenol-modified cyanate ester oligomer is an epoxy/phenol-modified cyanate ester oligomer obtainable by reacting 100 parts by weight of Component (A), 10 to 250 parts by weight of Component (B), and 0.4 parts by weight or more and less than 60 parts by weight of Component (C), and

Component (C) is additionally contained in a total amount of 2 to 60 parts by weight which is the sum of the amount with Component (C) to be used for formation of the epoxy/phenol-modified cyanate ester oligomer.

[Claim 34] A resin varnish for a printed wiring board obtainable by dissolving or dispersing the resin composition for printed wiring board according to any one of Claims 25 to 33 in a solvent.

[Claim 35] A prepreg for a printed wiring board which is obtainable by impregnating the resin composition for printed wiring board according to any one of Claims 25 to 33 or the resin varnish for a printed wiring board according to Claim 34 into a substrate, and drying at 80 to 200°C.

[Claim 36] A metal clad laminated board which is obtainable by laminating one or more of the prepreg for a printed wiring board according to Claim 35, laminating a metal foil on at least one surface thereof and pressurizing under heating.

[Detailed description of the invention]

[0001]

[Technical field to which the invention belongs]

The present invention relates to a resin composition for printed wiring board, and a varnish, a prepreg and a metal clad laminated board using the same. More specifically, it relates to a resin composition for printed wiring board which is used for electronic devices in which operating frequency exceeds 1 GHz, and a varnish, a prepreg and a metal clad laminated board using the same.

[0002]

[Prior art]

In recent years, in mobile communication devices represented by cellular phone or in net-work related electronic devices such as server, router, etc., it is required to transmit and treat huge amount of information with low loss and high speed, so that electric signals treated on the printed wiring board also become high frequencies. However, when a frequency is higher, electric signals likely decreased, so that it is required to use a material having low transmission loss for a printed wiring board to be used in these fields of art. That is, in a high frequency band region of 1 GHz or higher, a material having excellent dielectric characteristics represented by low values in dielectric constant and dielectric dissipation factor is required to be used.

[0003]

In these backgrounds, it has been attracted attention to use a cyanate ester resin having excellent dielectric characteristics of a cured product in a resin composition for printed wiring board. Heretofore, it has been proposed a resin composition in which a generally used epoxy resin such as a bisphenol A type epoxy resin, a brominated bisphenol A type epoxy resin, a phenol novolac type epoxy resin and a cresol novolac type epoxy resin is formulated with a cyanate ester resin, and it has been known that

humidity resistance or heat resistance under humidity are improved than the case of a cyanate ester resin alone (for example, see Patent References 1 to 3). However, these resin compositions are inferior in dielectric characteristics than those in which no epoxy resin is formulated due to the effect of an epoxy resin.

[0004]

Moreover, according to the present inventors, a resin composition in which dielectric characteristics at high frequency band region is improved has been proposed as compared to the case where the above-mentioned generally used epoxy resin is utilized by selecting, as an epoxy resin, a specific epoxy resin such as a naphthalene skeleton-containing epoxy resin, an aralkylene skeleton-containing epoxy resin, a lower alkyl group substituted phenol salicylic aldehyde novolac type epoxy resin, and a dicyclopentadiene skeleton-containing epoxy resin, and formulating them with a cyanate ester resin (for example, see Patent References 4 to 6).

[0005]

Also, a resin composition having sufficient dielectric characteristics even when an epoxy resin is formulated has been proposed by the present inventors by modifying a cyanate ester resin with a specific monovalent phenol compound to prepare a phenol-modified cyanate ester resin composition, whereby dielectric characteristics possessed by a cyanate ester resin have been more improved (for example, see Patent References 7).

[0006]

However, in either of the above-mentioned resin compositions, humidity resistance or heat resistance of a cured product is improved than the case where a cyanate ester resin or a modified cyanate ester resin is used alone, but due to the effect of an epoxy resin, a dielectric constant and a dielectric dissipation factor at high frequency band region are increased, or stability of

dielectric characteristics relative to temperature is observed to be lowered (for example, increase in drift accompanied by temperature change of dielectric characteristics), so that the problems remain in the point of improving dielectric characteristics.

[0007]

In particular, in a multi-layered printed wiring board to be used for wireless base station equipment use or high speed server, router, etc., temperature of the printed wiring board during operation of the device sometimes becomes a high temperature of 85 to 90°C, whereby there are possibility of causing significant problems that a dielectric constant is fluctuated due to change in temperature, or mismatching in impedance or transmission error accompanied by increase in transmission loss occurs when a dielectric dissipation factor becomes high. Accordingly, necessity for a resin composition for printed wiring board excellent in dielectric characteristics including temperature-dependency has been increased.

[0008]

The present invention has been accomplished in view of the above circumstances, and an object thereof is to provide a resin composition for printed wiring board which has the same molding property and workability as those of a thermosetting resin material such as an epoxy resin, etc., and having excellent humidity resistance and heat resistance, and also shows particularly excellent dielectric characteristics at high frequency band and excellent stability of dielectric characteristics against change in temperature, and a varnish, a prepreg and a metal clad laminated board using the same.

[0009]

[Patent Reference 1]

Patent Publication No. S 46-41112

[Patent Reference 2]

Unexamined Patent Publication No. S 50-132099

[Patent Reference 3]

Unexamined Patent Publication No. S 57-143320

[Patent Reference 4]

Unexamined Patent Publication No. H 8-176273

[Patent Reference 5]

Unexamined Patent Publication No. H 8-176274

[Patent Reference 6]

Unexamined Patent Publication No. H 11-60692

[Patent Reference 7]

Unexamined Patent Publication No. 2001-240723

[0010]

[Means for solving the problems]

The present inventors have earnestly studied and as a result, they have found that a resin composition for printed wiring board which is improved in humidity resistance and has excellent dielectric characteristics at high frequency band, is a little in drift property against temperature change in dielectric characteristics, and shows an excellent stability, by using an epoxy resin having a biphenyl structure (hereinafter referred to as an epoxy resin containing a biphenyl structure in the molecule as at least one kind of an epoxy resin when an epoxy resin is formulated to a cyanate ester resin, to accomplish the present invention.

[0011]

in a cyanate ester resin composition into which the conventionally employed epoxy resin is formulated, an isocyanuric ring, an oxazolidinone ring, etc. which have higher polarity than a triazine ring are formed other than the triazine ring, so that it can be considered that dielectric characteristics (in particular, dielectric dissipation factor) are worsened. On the other hand, in the resin composition containing an epoxy resin containing a biphenyl structure of the present invention, a biphenyl group show hydrophobic property and low polarity, so that it can be considered that bad effects caused by using an

epoxy resin in combination on dielectric characteristics are reduced than the conventional one. Also, a biphenyl skeleton with a brittle structure is introduced into the cured product, so that it can be considered that a temperature-dependency of dielectric characteristics is a little due to low mobility of a molecular chain particularly at a high temperature region.

[0012]

Moreover, the resin composition for printed wiring board of the present invention is excellent in heat resistance at the time of absorbing moisture and higher strength and elongation at a glass state region or elongation at a high temperature region as compared with the case where a cyanate ester resin, etc. is used alone or the case where the conventional epoxy resin is used in combination with a cyanate ester resin, so that it is preferred for the uses such as a laminated board to be used for a multilayered printed wiring board of ten-layers or more to which crack resistance at the time of drilling processing or reflow, and severe heat resistance and for a prepreg.

[0013]

Thus, the present invention relates to a resin composition for printed wiring board characterized in comprising (A) a cyanate ester compound having 2 or more cyanate groups in the molecule and/or a prepolymer thereof, (B) an epoxy resin containing at least one kind of an epoxy resin having a biphenyl structure in the molecule; moreover, the above resin composition for printed wiring board comprising further (C) a monovalent phenol compound. The present invention relates to a varnish, a prepreg and a metal clad laminated board using the resin composition for printed wiring board.

[0014]

Moreover, the present invention relates to a resin composition for printed wiring board characterized in

comprising (A) a phenol-modified cyanate ester oligomer obtainable by reacting a cyanate ester compound having 2 or more cyanate groups in the molecule and/or a prepolymer thereof, (C) a monovalent phenol compound, and (B) an epoxy resin containing at least one kind of an epoxy resin having a biphenyl structure in the molecule, and a varnish, a prepreg and a metal clad laminated board using the same.

[0015]

Also, the present invention relates to a resin composition for printed wiring board characterized in comprising (A) a phenol-modified cyanate ester oligomer obtainable by reacting a cyanate ester compound having 2 or more cyanate groups in the molecule and/or a prepolymer thereof, and (B) an epoxy resin containing at least one kind of an epoxy resin having a biphenyl structure in the molecule, and (C) a monovalent phenol compound, and a varnish, a prepreg and a metal clad laminated board using the same.

[0016]

[Embodiments of the invention]

In the following, the present invention is explained in detail.

[0017]

The first embodiment of the present invention is a composition comprising (A) a cyanate ester compound having 2 or more cyanate groups in the molecule and/or a prepolymer thereof, and (B) an epoxy resin containing at least one kind of an epoxy resin having a biphenyl structure.

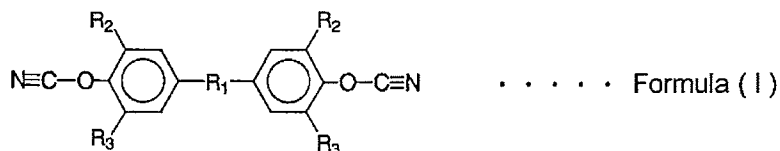
[0018]

(A) The cyanate ester compound having 2 or more cyanate groups in the molecule of the present invention is not specifically limited. If two or more cyanate groups are present in the molecule, it is possible to cure the composition by cross-linking. For example, there may be mentioned a cyanate ester compound represented by the

formula (I):

[0019]

[Formula 25]

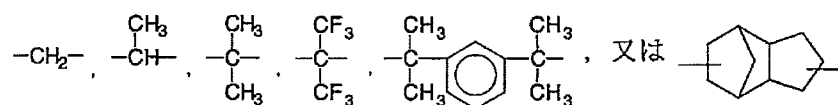


[0020]

(wherein R₁ represents

[0021]

[Formula 26]



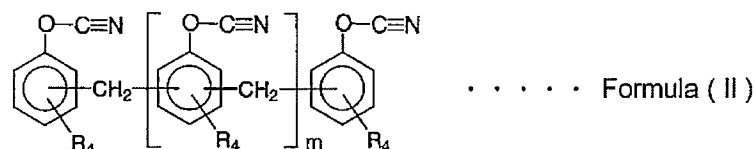
[0022]

R₂ and R₃ each represent a hydrogen atom or an alkyl group having 1 to 4 carbon atoms, and each may be the same or different from each other)

and a cyanate ester compound represented by the formula (II):

[0023]

[Formula 27]



[0024]

(wherein R₄ represents a hydrogen atom or an alkyl group having 1 to 4 carbon atoms, m represents an integer of 1 to 7.)

[0025]

A prepolymer of the cyanate ester compound having 2 or more cyanate groups in the molecule of Component (A) is

not specifically limited. Here, the prepolymer means a cyanate ester oligomer in which cyanate ester compounds form a triazine ring by cyclization reaction, and may be mentioned mainly 3, 5, 7, 9 and 11-oligomers of the cyanate ester compounds. In the prepolymer, a conversion rate of the cyanate group is not specifically limited, and a prepolymer in which they are converted generally in the range of 20 to 70% is preferably used, more preferably 30 to 65%. For example, there may be mentioned a prepolymer of the cyanate ester compound represented by the formula (I) or (II).

[0026]

Preferred examples of Component (A) may be mentioned 2,2-bis(4-cyanatophenyl)propane, bis(4-cyanatophenyl)ethane, bis(3,5-dimethyl-4-cyanatophenyl)methane, 2,2-bis(4-cyanatophenyl)-1,1,1,3,3,3-hexafluoropropane, α,α' -bis(4-cyanatophenyl)-m-diisopropylbenzene, a cyanate ester compound of a phenol-added dicyclopentadiene polymer, a phenol novolac type cyanate ester compound and a cresol novolac type cyanate ester compound, and a prepolymer thereof, etc., and preferably 2,2-bis(4-cyanatophenyl)propane, α,α' -bis(4-cyanatophenyl)-m-diisopropylbenzene, bis(3,5-dimethyl-4-cyanatophenyl)methane, and a prepolymer thereof. They may be used alone or in combination of two or more kinds.

[0027]

The epoxy resin containing at least one kind of (B) an epoxy resin containing a biphenyl structure of the present invention is not specifically limited so long as it contains an epoxy resin containing a biphenyl structure as an essential component. For example, it may be either of an epoxy resin comprising one kind of an epoxy resin containing a biphenyl structure, an epoxy resin comprising two or more kinds of epoxy resins containing a biphenyl structure, or an epoxy resin comprising a combination of at least one kind of an epoxy resin containing a biphenyl

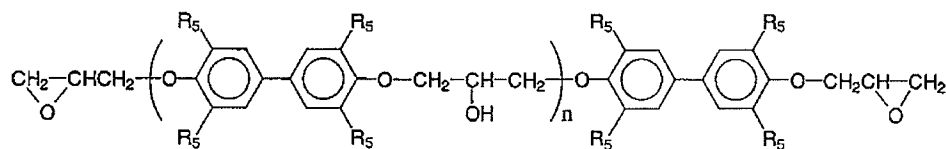
structure and at least one kind of another epoxy resin. Incidentally, an epoxy resin having a biphenyl skeleton and other skeleton is classified into an epoxy resin containing a biphenyl structure in the present invention.

[0028]

The epoxy resin containing a biphenyl structure is not specifically limited, and may be mentioned, for example, an epoxy resin represented by the formula (III):

[0029]

[Formula 28]



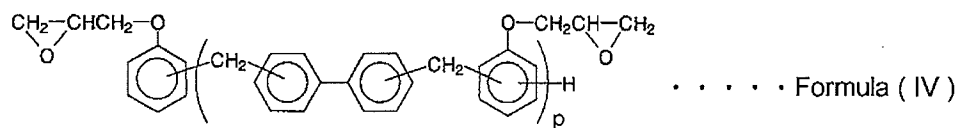
. Formula (III)

[0030]

(wherein R₅ each represent a hydrogen atom or a methyl group, n represents an integer of 0 to 6) and an epoxy resin represented by the formula (IV):

[0031]

[Formula 29]



. Formula (IV)

[0032]

(wherein p represents an integer of 1 to 5.)

[0033]

In the epoxy resin represented by the formula (III), n is preferably 0 to 5, more preferably 0 to 3, more preferably 0 or 1, particularly preferably 0. Also, a mixture of epoxy resins of the formula (III) in which values of n are different from each other may be used. There may be specifically mentioned biphenol diglycidyl ether, and 3,3',5,5'-tetramethylbiphenol diglycidyl ether,

etc., and as the epoxy resin represented by the formula (IV), there may be mentioned a biphenyl aralkylene novolac type epoxy resin. Also, a mixture of epoxy resins of the formula (IV) in which values of p are different from each other may be used.

[0034]

When Component (B) is a component in which at least one of the epoxy resin containing a biphenyl structure and at least one of an epoxy resin other than the epoxy resin containing a biphenyl structure are combined, the other epoxy resin is not specifically limited, and there may be mentioned, for example, a bisphenol A type epoxy resin, a bisphenol F type epoxy resin, a brominated bisphenol A type epoxy resin, a phenol novolac type epoxy resin, a cresol novolac type epoxy resin, a brominated phenol novolac type epoxy resin, a bisphenol A novolac type epoxy resin, a naphthalene skeleton-containing epoxy resin, an aralkylene skeleton-containing epoxy resin, a phenol salicylic aldehyde novolac type epoxy resin, a lower alkyl group-substituted phenol salicylic aldehyde novolac type epoxy resin and a dicyclopentadiene skeleton-containing epoxy resin, etc. Of these, a phenol novolac type epoxy resin and a cresol novolac type epoxy resin are suitably used in combination in view of high glass transition temperature (T_g) and cost, and for the purpose of providing flame resistance, a brominated bisphenol A type epoxy resin and a brominated phenol novolac type epoxy resin, etc. are suitably used in combination.

[0035]

A formulation amount of Component (B) is preferably 10 to 250 parts by weight based on 100 parts by weight Component (A) in view of humidity resistance under severe conditions, improvement in heat resistance, strength and elongation at the time of absorbing moisture, and dielectric characteristics at high frequency band region. A formulation amount of Component (B) is more preferably 10

to 150 parts by weight, particularly preferably 10 to 100 parts by weight. In view of dielectric characteristics, a ratio of the epoxy resin containing a biphenyl structure in Component (B) is preferably 50 % by weight or more, more preferably 70 % by weight or more, particularly preferably 100 % by weight, that is, whole of Component (B) is an epoxy resin containing a biphenyl structure.

[0036]

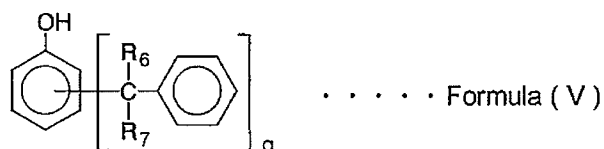
To the resin composition of the first embodiment, (C) a monovalent phenol compound may be formulated. By formulating Component (C), an amount of an unreacted cyanate group in the cured product can be reduced, so that it is preferred in the points of humidity resistance and dielectric characteristics.

[0037]

Component (C) is not specifically limited, and there may be mentioned, for example, a monovalent phenol compound represented by the formula (V):

[0038]

[Formula 30]



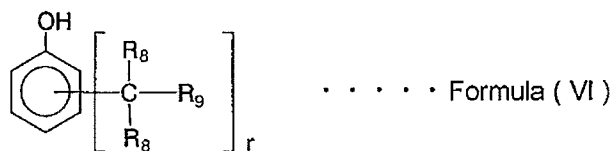
[0039]

(wherein R_6 and R_7 each represent a hydrogen atom or a methyl group, each may be the same or different from each other, and q represents an integer of 1 to 3)

and a monovalent phenol compound represented by the formula (VI):

[0040]

[Formula 31]

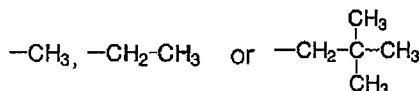


[0041]

(wherein R_8 represents a hydrogen atom or a methyl group, R_9 represents

[0042]

[Formula 32]



[0043]

and r represents an integer of 1 or 2.)

[0044]

As the monovalent phenol compound represented by the formula (V), there may be mentioned p-(α -cumyl)phenol, mono-, di- or tri-(α -methylbenzyl)phenol. As the monovalent phenol compound represented by the formula (VI), there may be mentioned p-tert-butylphenol, 2,4- or 2,6-di-tert-butylphenol, p-tert-amylphenol and p-tert-octylphenol. These monovalent phenol compounds may be used alone or in combination of two or more kinds.

[0045]

A formulation amount of Component (C) of the present invention is preferably in the range of 2 to 60 parts by weight based on 100 parts by weight of Component (A), more preferably 3 to 45 parts by weight, particularly preferably 4 to 30 parts by weight. When Component (C) is formulated in this range, it is preferred in the point of dielectric characteristics, in particular, a product having a sufficiently low dielectric dissipation factor particularly at a high frequency band region can tend to be obtained, and sufficient effects can be obtained in the point of

humidity resistance, and there is a tendency of not exerting bad effect on heat resistance, etc. at the time of absorbing moisture.

[0046]

To the resin composition of the first embodiment, a metal series catalyst is preferably formulated. The metal series catalyst acts as a promoting agent of a self-polymerization reaction of Component (A), and in the reaction of Component (A) and Component (C) when Component (C) is formulated, and as a curing accelerator at the time of producing laminated boards, and there may be mentioned, for example, a metal salt or chelate complex of a transition metal or a metal belonging to Group 12. As the metal, there may be mentioned, for example, copper, cobalt, manganese, iron, nickel, zinc, etc., and as the salt thereof, there may be mentioned, for example, a metal salt such as a carboxylate (preferably 2-ethylhexanoate, naphthenate), etc., and as the chelate complex, there may be mentioned, for example, an acetylacetone complex. These metal series catalysts may be used alone or in combination of two or more kinds. Also, the promoting agent in the self-polymerization reaction of Component (A), and in the reaction of Component (A) and Component (C), and the curing accelerator at the time of producing laminated boards may be the same or different metal series catalyst from each other.

[0047]

An amount of the metal series catalyst is preferably 1 to 300 ppm based on the amount of Component (A) in terms of weight, more preferably 1 to 200 ppm, particularly preferably 2 to 150 ppm. When a metal series catalyst is formulated in this range, reactivity and curing property is sufficient, and curing rate is suitable. Addition of the metal series catalyst may be carried out at once or may be divided into a plural number of times.

[0048]

In the resin composition of the first embodiment, a compound which has a catalytic function of promoting the reaction of a glycidyl group of Component (B) may be formulated. More specifically, there may be mentioned an alkali metal compound, an alkaline earth metal compound, an imidazole compound, an organic phosphorus compound, a secondary amine, a tertiary amine, a quaternary ammonium salt and the like. These compounds may be used alone or in combination of two or more kinds.

[0049]

In the resin composition of the first embodiment, if necessary, an additive such as a flame retardant, a filler, etc. may be formulated in a range which does not worsen dielectric characteristics or characteristics such as heat resistance, etc. of the cured product.

[0050]

The flame retardant to be formulated depending on necessity is not specifically limited, and is preferably a flame retardant having no reactivity with a cyanate group. Here, the terms having no reactivity with a cyanate group mean that a flame retardant is added to a resin composition for printed wiring board, even when they are mixed in a range of 300°C or lower, the flame retardant does not react with a cyanate group of the cyanate ester compound and is to be contained in a resin composition for printed wiring board as such in a dispersed or dissolved state. In this reaction, a reaction of a flame retardant when the resin composition is burned under heating is not included. In general, production and use of the resin composition for printed wiring board, and the varnish, prepreg, metal clad laminated board, printed wiring board, etc. using the same are carried out in the range of 300°C or lower.

[0051]

As such a flame retardant, there may be mentioned a flame retardant substantially having no alcoholic hydroxyl group, phenolic hydroxyl group, amino group or maleimide

group, which are known as a group which reacts with a cyanate group. Here, the terms "substantially having no" include the case where the flame retardant never contains these groups and the case where even when the flame retardant contains these groups but there is no interaction with the cyanate ester compound (for example, it is the case where the flame retardant is a polymer having a large molecular weight, and these groups exist at the end of the molecule, so that there is no effect as a functional group).

[0052]

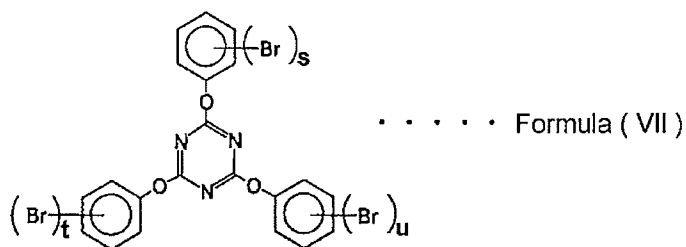
Incidentally, with regard to a flame retardant classified into an epoxy resin including a brominated epoxy resin such as a brominated bisphenol A type epoxy resin and a brominated phenol novolac type epoxy resin, etc., it is classified in Component (B) in the present invention. Provided that, a flame retardant classified into an epoxy compound having only one glycidyl group reacts with a cyanate ester compound, and can be inserted into a triazine ring or an isocyanuric ring, but if it is a suitable formulation amount, effects on dielectric characteristics are considered to be little so that it may be used as a flame retardant.

[0053]

Specific flame retardant may be mentioned, for example, 1,2-dibromo-4-(1,2-dibromoethyl)cyclohexane, tetrabromocyclooctane, hexabromocyclododecane, bis(tribromophenoxy)ethane, a brominated polyphenylene ether, brominated polystyrene, and a brominated triphenylcyanurate flame retardant represented by the formula (VII):

[0054]

[Formula 33]



[0055]

(wherein s, t and u each represent an integer of 1 to 5, and each may be the same value or different from each other)

and the like, and in the point of dielectric characteristics, 1,2-dibromo-4-(1,2-dibromoethyl)cyclohexane, tetrabromocyclooctane, hexabromocyclododecane and 2,4,6-tris-(tribromophenoxy)-1,3,5-triazine are preferred.

[0056]

A formulation amount of the flame retardant is preferably set to 5 to 100 parts by weight based on 100 parts by weight of Component (A), Component (B) and Component (C) (when they are formulated) in total, more preferably 5 to 80 parts by weight, particularly preferably 5 to 60 parts by weight. When it is formulated in this range, heat resistance is sufficient in the resin composition, and heat resistance of the cured product is also preferred.

[0057]

The filler to be formulated depending on necessity is not specifically limited, it is usually an inorganic filler, and there may be mentioned, for example, alumina, titanium oxide, mica, silica, beryllia, barium titanate, potassium titanate, strontium titanate, calcium titanate, aluminum carbonate, aluminum hydroxide, aluminum silicate, potassium carbonate, calcium silicate, magnesium silicate, silicon nitride, boron nitride, clay (calcined clay, etc.), talc, aluminum borate, aluminum borate, silicon carbide, etc. These inorganic fillers may be used alone or in combination of two or more kinds. Also, a shape, a

particle size, etc. of the inorganic filler are not specifically limited, and it is usually having a particle size of 0.01 to 50 μm , preferably those having 0.1 to 15 μm . Moreover, a formulation amount of these inorganic filler is not specifically limited, and is preferably 1 to 1000 parts by weight based on 100 parts by weight of Component (A), Component (B) and Component (C) (when they are formulated) in total, more preferably 1 to 800 parts by weight.

[0058]

The resin composition of the first embodiment can be produced by formulating Component (A), Component (B) and occasionally Component (C) or other additive(s) by the conventionally known method, and mixing.

[0059]

The second embodiment of the present invention comprises a composition containing a phenol-modified cyanate ester oligomer obtained by reacting (A) a cyanate ester compound having 2 or more cyanate groups in the molecule and/or a prepolymer and (C) a monovalent phenol compound, and an epoxy resin containing at least one kind of (B) an epoxy resin containing a biphenyl structure. By previously modifying Component (A) with phenol and formulating an epoxy resin which contains an epoxy resin having a biphenyl structure, an amount of the cyanate group remained in the cured product can be reduced, and humidity resistance and dielectric characteristics can be more improved.

[0060]

The phenol-modified cyanate oligomer becomes a mixed oligomer comprising, for example, a cyanate ester oligomer in which Component (A) solely forms a triazine ring by cyclization reaction, an imidecarbonated-modified oligomer in which a phenolic hydroxyl group of Component (C) is added to a cyanate group of Component (A), and/or a modified oligomer (in this case, among the three chains

extended from the triazine ring, one or two thereof is/are replaced by the molecule derived from Component (C)) in which one or two of Component (C) is introduced into the structure of a triazine ring formed by sole cyclization of Component (A).

[0061]

With regard to examples of Component (A) to be used for formation of the phenol-modified cyanate ester oligomer and examples of Component (C), and examples of Component (B), descriptions of Component (A), Component (C), and Component (B) with regard to the first embodiment are applied to.

[0062]

Component (C) to be used for formation of the phenol-modified cyanate ester oligomer is preferably within the range of 2 to 60 parts by weight based on 100 parts by weight of Component (A), more preferably 3 to 45 parts by weight, particularly preferably 4 to 30 parts by weight.

[0063]

A formulation amount of Component (B) of the present invention is preferably 10 to 250 parts by weight based on 100 parts by weight of Component (A) to be used for formation of the phenol-modified cyanate ester oligomer, more preferably 10 to 150 parts by weight, particularly preferably 10 to 100 parts by weight. In the point of dielectric characteristics, a ratio of the epoxy resin containing a biphenyl structure in Component (B) is preferably 50 % by weight or more, more preferably 70 % by weight or more, particularly preferably 100 % by weight, i.e., all the Component (B) is the epoxy resin containing a biphenyl structure.

[0064]

The resin composition of the second embodiment may further contain Component (C), and in such a case, a sum of said Component (C), and Component (C) to be used for formation of the phenol-modified cyanate ester oligomer is

preferably within the range of 2 to 60 parts by weight based on 100 parts by weight of Component (A). For example, Component (C) is previously reacted in the range of 0.4 parts by weight or more and less than 60 parts by weight based on 100 parts by weight of Component (A) to prepare a phenol-modified cyanate ester oligomer, and then, Component (C) is additionally formulated so that a sum of the amount thereof with that of Component (C) to be used for formation of the phenol-modified cyanate ester oligomer becomes within the range of 2 to 60 parts by weight. When Component (C) is previously reacted in the range of 2 to 60 parts by weight based on 100 parts by weight of Component (A) to obtain a phenol-modified cyanate ester oligomer, additional Component (C) may not be formulated, or may be formulated so that a sum of the amount thereof with that of Component (C) to be used for formation of the phenol-modified cyanate ester oligomer becomes within the range of 2 to 60 parts by weight. Incidentally, in the above-mentioned case, Component (C) to be used for formation of the phenol-modified cyanate ester oligomer, and additional Component (C) may be the same or different from each other, and each may be used in combination of two or more kinds in admixture.

[0065]

The phenol-modified cyanate ester oligomer can be prepared, for example, Component (A) and Component (C) are mixed in a solvent such as toluene, xylene, mesitylene, etc., and heating to 70 to 120°C for 0.5 to 10 hours. At this time, the metal series catalyst described in the first embodiment may be added to the mixture. These metal series catalysts are to promote modification by phenol. Incidentally, the phenol-modified cyanate ester oligomer can be made, for example, a conversion of the initial cyanate group of 20 to 70%, preferably in the range of 30 to 65%.

[0066]

The resin composition of the second embodiment can be

obtained by formulating Component (B) to the phenol-modified cyanate ester oligomer obtained as mentioned above, and if necessary, Component (C) is further formulated to the mixture. To the above composition, similarly as in the resin composition of the first embodiment, a metal series catalyst, a compound having a catalytic function which promotes the reaction of a glycidyl group of the epoxy resin, a flame retardant, a filler, other additives, etc. may be formulated, and with regard to specific examples, preferred examples, formulation amounts, and a preparation method of the resin composition, the descriptions with regard to the first embodiment can be similarly applied to.

[0067]

The third embodiment of the present invention is a composition containing (A) a cyanate ester compound having 2 or more cyanate groups in the molecule and/or a prepolymer thereof, (B) an epoxy resin containing at least one kind of an epoxy resin containing a biphenyl structure, and (C) an epoxy/phenol-modified cyanate ester oligomer obtained by reacting a monovalent phenol compound. By carrying out phenol-modification and epoxy-modification, a desired melting viscosity can be provided, an amount of the cyanate group remained in the cured product is reduced, and improvement in humidity resistance and dielectric characteristics can be accomplished.

[0068]

Examples of Component (A), Component (B) and Component (C) to be used for formation of the epoxy/phenol-modified cyanate ester oligomer, the descriptions of Component (A), Component (B) and Component (C) with regard to the first embodiment can be applied to. For formation of the epoxy/phenol-modified cyanate ester oligomer, Component (B) is preferably 10 to 250 parts by weight based on 100 parts by weight of Component (A), more preferably 10 to 150 parts by weight, particularly preferably 10 to 100 parts by weight. In the point of dielectric

characteristics, a ratio of the epoxy resin containing a biphenyl structure in Component (B) is preferably 50 % by weight or more, more preferably 70 % by weight or more, particularly preferably 100 % by weight, i.e., all the Component (B) is the epoxy resin containing a biphenyl structure. In the formation of the epoxy/phenol-modified cyanate ester oligomer, Component (C) is preferably within the range of 2 to 60 parts by weight based on 100 parts by weight of Component (A), more preferably 3 to 45 parts by weight, particularly preferably 4 to 30 parts by weight.

[0069]

The resin composition of the third embodiment may contain further Component (C), and in such a case, a sum of said Component (C), and Component (C) to be used for formation of the epoxy/phenol-modified cyanate ester oligomer is preferably within the range of 2 to 60 parts by weight based on 100 parts by weight of Component (A). For example, 10 to 250 parts by weight of Component (B) and 0.4 parts by weight or more and less than 60 parts by weight of Component (C) based on 100 parts by weight of Component (A) are provisionally reacted to prepare an epoxy/phenol-modified cyanate ester oligomer, Component (C) may be additionally formulated in such an amount that a sum of the same with Component (C) to be used for formation of the epoxy/phenol-modified cyanate ester oligomer becomes within the range of 2 to 60 parts by weight. Component (C) to be used for formation of the epoxy/phenol-modified cyanate ester oligomer, and additional Component (C) may be the same or different from each other, and each may be used in combination of two or more kinds in admixture.

[0070]

The epoxy/phenol-modified cyanate ester resin composition can be prepared by, for example, dissolving Component (A), Component (B) and Component (C) in a solvent such as toluene, xylene, mesitylene, etc., and heating at 70 to 120°C for 0.5 to 10 hours. At this time, the metal

series catalyst described in the first embodiment may be added. These metal series catalysts are to promote modification by phenol. Incidentally, the epoxy/phenol-modified cyanate ester oligomer may be made, for example, a conversion of the initial cyanate group of 20 to 70%, preferably within the range of 30 to 65%.

[0071]

To the resin composition of the third embodiment, similarly as in the resin composition of the first embodiment, a metal series catalyst, a compound having a catalytic function which promotes the reaction of a glycidyl group of the epoxy resin, a flame retardant, a filler, other additives, etc. may be formulated, and with regard to specific examples, preferred examples, formulation amounts, and a preparation method of the resin composition, the descriptions with regard to the first embodiment can be similarly applied to.

[0072]

By using the resin composition for printed wiring board of the first to the third embodiment according to the present invention, a prepreg for a printed wiring board or a metal clad laminated board can be produced according to the conventionally known method. For example, the resin composition for printed wiring board of the present invention is as such, or in a form of a varnish in which they are dissolved or dispersed in a solvent, impregnated into a substrate such as a glass cloth, etc., and then, drying in a drying oven usually at a temperature of 80 to 200°C (provided that, when a solvent is used, it is set at a temperature capable of volatilizing the solvent or higher), preferably at 100 to 180°C, for 3 to 30 minutes, preferably 3 to 15 minutes to obtain a prepreg. Then, this prepreg is laminated with a plural number of sheets, a metal foil(s) is/are provided on one surface or both surfaces thereof, and molding under heating to produce a both surface or one surface metal clad laminated board.

[0073]

Incidentally, the solvent to be used in the above-mentioned varnishing treatment is not specifically limited, and there may be mentioned a solvent, for example, alcohols such as methanol, ethanol, ethylene glycol, ethylene glycol monomethyl ether, etc., ketones such as acetone, methyl ethyl ketone, methyl isobutyl ketone, cyclohexanone, etc., aromatic hydrocarbons such as toluene, xylene, mesitylene, etc., esters such as methoxyethyl acetate, ethoxyethyl acetate, butoxyethyl acetate, ethyl acetate, etc., amides such as N-methylformamide, N,N-dimethylformamide, N,N-dimethylacetamide, N-methylpyrrolidone, etc. In particular, aromatic hydrocarbons such as toluene, xylene, mesitylene, etc. are more preferred. They may be used alone or in combination of two or more kinds.

[0074]

The resin composition for printed wiring board of the present invention, and the varnish, prepreg and metal clad laminated board using the same can be used for a printed wiring board which can be used for information communication-related devices (parts such as a filter, VCO, etc. included in mobile communication devices, or signal processor, power amplifier and antenna which constitutes wireless base station equipments, or a high speed computer which exceeds a clock frequency of 1 GHz such as a server, router and microprocessor, etc.) which are required to have higher frequencies and high speed in signals.

[0075]

[Example]

In the following, the present invention is explained in more detail by referring to specific examples, but the present invention is not limited by these. The resin varnishes for metal clad laminate were prepared according to the formulations shown in Table 1.

[0076]

Example 1

In a 3-liter four-necked separable flask equipped with a thermometer, a condenser and a stirring device, 833 g of toluene, 1000 g of a prepolymer (Arocy B-10, available from Ciba Geigy AG) of 2,2-bis(4-cyanatophenyl)propane and 547 g of 3,3',5,5'-tetramethylbiphenol diglycidyl ether (a tetramethylbiphenyl type epoxy resin, YX-4000, available from Japan Epoxy Resin Co.) were charged, and the mixture was heated to 80°C and dissolved under stirring. Then, after confirmation of dissolution, the mixture was cooled to room temperature; 1.25 g of zinc naphthenate (available from Wako Pure Chemical Industries, Ltd.) was formulated in the mixture as a curing accelerator to prepare a resin varnish having a non-volatile concentration of about 65 % by weight.

[0077]

Example 2

In a 3-liter four-necked separable flask equipped with a thermometer, a condenser and a stirring device, 780 g of toluene, 1000 g of a prepolymer (Arocy M-30, available from Ciba Geigy AG) of bis(3,5-dimethyl-4-cyanatophenyl)-methane of 2,2-bis(4-cyanatophenyl)propane and 447 g of a mixed biphenyl type epoxy resin (YL-612H, available from Japan Epoxy Resin Co.) comprising biphenol diglycidyl ether and 3,3',5,5'-tetramethylbiphenol diglycidyl ether were charged, and the mixture was heated to 80°C and dissolved under stirring. Then, after confirmation of dissolution, the mixture was cooled to room temperature; 1.25 g of zinc naphthenate (available from Wako Pure Chemical Industries, Ltd.) was formulated in the mixture as a curing accelerator to prepare a resin varnish having a non-volatile concentration of about 65 % by weight.

[0078]

Example 3

In a 3-liter four-necked separable flask equipped with a thermometer, a condenser and a stirring device, 885 g of toluene, 1000 g of α,α' -bis(4-cyanatophenyl)-m-

diisopropylbenzene (RTX-366, available from Ciba Geigy AG), and 586 g of a biphenyl aralkylene novolac type epoxy resin (NC-3000S-H, available from Nippon Kayaku Co., Ltd.) were charged, and the mixture was heated to 80°C and dissolved under stirring. Then, after confirmation of dissolution, the mixture was cooled to room temperature, 62 g of p-tert-octylphenol (available from Wako Pure Chemical Industries, Ltd.) and 0.4 g of zinc naphthenate (available from Wako Pure Chemical Industries, Ltd.) as a curing accelerator were formulated in the mixture to prepare a resin varnish having a non-volatile concentration of about 65 % by weight.

[0079]

Example 4

In a 3-liter four-necked separable flask equipped with a thermometer, a condenser and a stirring device, 438 g of toluene, 1000 g of 2,2-bis(4-cyanatophenyl)propane (Arocy B-10, available from Ciba Geigy AG) and 30 g of p-(α -cumyl)phenol (available from Tokyo Kasei Kogyo Co., Ltd.) were charged, and after confirmation of dissolution and the liquid temperature was maintained at 110°C, 0.3 g of manganese naphthenate (available from Wako Pure Chemical Industries, Ltd.) was formulated in the mixture as a reaction promoter, and the mixture was reacted under heating for about 1 hour to synthesize a phenol-modified cyanate oligomer solution. Then, the reaction solution was cooled, and when the inner temperature reached to 80°C, 457 g of methyl ethyl ketone and 547 g of 3,3',5,5'-tetramethylbiphenol diglycidyl ether (YX-4000, available from Japan Epoxy Resin Co.) were formulated in the mixture under stirring. After confirmation of the dissolution, the mixture was cooled to room temperature, and 92 g of p-(α -cumyl)phenol and 0.15 g of zinc naphthenate (available from Wako Pure Chemical Industries, Ltd.) as a curing accelerator were formulated in the mixture to prepare a resin varnish having a non-volatile concentration of about 65 %

by weight.

[0080]

Comparative Example 1

In the same manner as in Example 1 except for using a bisphenol A type epoxy resin (DER-331L, available from Dow Chemical) in place of 3,3',5,5'-tetramethylbiphenol diglycidyl ether and formulating in a formulation amount as shown in Table 1, the procedure was carried out as in Example 1 to prepare a resin varnish having a non-volatile concentration of about 65 % by weight.

[0081]

Comparative Example 2

In the same manner as in Example 1 except for using a phenol novolac type epoxy resin (N-770, available from Dainippon Ink and Chemicals Incorporated) in place of 3,3',5,5'-tetramethylbiphenol diglycidyl ether and formulating in a formulation amount as shown in Table 1, the procedure was carried out as in Example 1 to prepare a resin varnish having a non-volatile concentration of about 65 % by weight.

[0082]

Comparative Example 3

In the same manner as in Example 1 except for using a bisphenol A novolac type epoxy resin (N-865, available from Dainippon Ink and Chemicals Incorporated) in place of 3,3',5,5'-tetramethylbiphenol diglycidyl ether and formulating in a formulation amount as shown in Table 1, the procedure was carried out as in Example 1 to prepare a resin varnish having a non-volatile concentration of about 65 % by weight.

[0083]

Comparative Example 4

In the same manner as in Example 1 except for using a methyl group and tert-butyl group-substitution type phenol salicylic aldehyde novolac type epoxy resin (TMH-574, available from Sumitomo Chemical Co., Ltd.) in place of

3,3',5,5'-tetramethylbiphenol diglycidyl ether and formulating in a formulation amount as shown in Table 1, the procedure was carried out as in Example 1 to prepare a resin varnish having a non-volatile concentration of about 65 % by weight.

[0084]

Comparative Example 5

In the same manner as in Example 1 except for using a dicyclopentadiene skeleton-containing epoxy resin (HP-7200, available from Dainippon Ink and Chemicals Incorporated) in place of 3,3',5,5'-tetramethylbiphenol diglycidyl ether and formulating in a formulation amount as shown in Table 1, the procedure was carried out as in Example 1 to prepare a resin varnish having a non-volatile concentration of about 65 % by weight.

[0085]

Comparative Example 6

In the same manner as in Example 1 except for using, a β -naphtholaralkylene type epoxy resin (ESN-175, available from Nippon Steel Chemical Group) in place of 3,3',5,5'-tetramethylbiphenol diglycidyl ether and formulating in a formulation amount as shown in Table 1, the procedure was carried out as in Example 1 to prepare a resin varnish having a non-volatile concentration of about 65 % by weight.

[0086]

[Table 1]

Table 1

Item	Example				Comparative example					
	1	2	3	4	1	2	3	4	5	6
Cyanate ester compound	1000	-	-	-	1000	1000	1000	1000	1000	1000
	-	1000	-	-	-	-	-	-	-	-
	-	-	1000	-	-	-	-	-	-	-
	-	-	-	1000	-	-	-	-	-	-
Phenol compound	-	-	62	-	-	-	-	-	-	-
	-	-	-	30	-	-	-	-	-	-
	-	-	-	92	-	-	-	-	-	-
Epoxy resin	547	-	-	547	-	-	-	-	-	-
	-	447	-	-	-	-	-	-	-	-
	-	-	586	-	-	-	-	-	-	-
	-	-	-	-	532	-	-	-	-	-
	-	-	-	-	-	544	-	-	-	-
	-	-	-	-	-	-	540	-	-	-
	-	-	-	-	-	-	-	622	-	-
	-	-	-	-	-	-	-	-	735	-
	-	-	-	-	-	-	-	-	-	700
	-	-	-	-	-	-	-	-	-	-
Curing accelerator (Reaction catalyst)	-	-	-	0.3	-	-	-	-	-	-
	1.25	1.25	0.4	0.15	1.25	1.25	1.25	1.25	1.25	1.25
Non-volatile concentration of varnish (% by weight)	65	65	65	65	65	65	65	65	65	65

[0087]

The resin varnishes obtained in Examples 1 to 4 and Comparative examples 1 to 6 were each impregnated into a glass cloth (E glass) with a thickness of 0.15 mm, and then, the material was dried at 160°C for 5 to 15 minutes to obtain the respective prepregs with a resin solid content of 52% by weight. Then, four sheets of this prepregs were laminated, and copper foils with a thickness of each 18 μ m were provided on the both outermost layers, and molding was carried out under the pressing conditions of 230°C for 70 minutes and 2.5MPa by heating and pressure to prepare a both-surface copper clad laminated board. With regard to the obtained copper clad laminated board, dielectric characteristics, copper foil peeling strength, solder heat resistance, water absorption rate, bending characteristics, thermal expansion coefficient (α) and Tg (glass transition temperature) were evaluated. The evaluation results are shown in Table 2.

[0088]

Evaluation methods of the characteristics of the copper clad laminated boards are as shown below.

Dielectric constant (ϵ_r) and dielectric dissipation factor ($\tan \delta$) of the copper clad laminated boards were measured by a triplate line resonator method using a vector type network analyzer. Incidentally, the measurement conditions are made a frequency: 1 GHz, measurement temperatures: room temperature (25°C) and 90°C.

Thermal expansion coefficient (α) and Tg of the copper clad laminated boards (whole surface-copper foil etched product) were measured by TMA.

Copper foil peeling strength of the copper clad laminated boards was measured according to the copper clad laminated boards test standard JIS-C-6481.

Solder heat resistance of the copper clad laminated boards (whole surface-copper foil etched product) was examined by maintaining in a pressure cooker tester (conditions: 121°C, 2.2 atm) for 1 to 5 hours, then,

immersing in a melting solder at 260°C and 288°C for 20 seconds, and the appearance thereof was judged with naked eyes. No abnormality in the table means that there is no occurrence of measling or blister.

Water absorption rate of the copper clad laminated boards (whole surface-copper foil etched product) was calculated from a weight difference between the normal state and after maintaining in a pressure cooker tester (conditions: 121°C, 2.2 atm) for 5 hours (unit: % by weight).

Bending characteristics of the copper clad laminated boards (whole surface-copper foil etched product) were obtained by measuring bending modulus at room temperature and at 200°C according to copper clad laminated boards test standard JIS-C-6481, breaking strength and breaking elongation at room temperature, and yield strength and yield elongation at 200°C.

[0089]

[Table 2]

Table 2

Item	Example				Comparative example					
	1	2	3	4	1	2	3	4	5	6
Copper foil peeling strength (kN/m)	1.5	1.5	1.5	1.5	1.5	1.5	1.5	1.5	1.4	1.5
ϵr	3.62	3.55	3.45	3.58	3.67	3.68	3.66	3.64	3.65	3.64
	3.64	3.52	3.47	3.60	3.74	3.74	3.75	3.70	3.70	3.70
$\tan \delta$	0.0064	0.0062	0.0045	0.0059	0.0082	0.0085	0.0088	0.0067	0.0069	0.0068
	0.0069	0.0067	0.0051	0.0064	0.0101	0.0105	0.0108	0.0079	0.0081	0.0080
Solder heat resistance (260°C)	3/3	3/3	3/3	3/3	3/3	3/3	3/3	3/3	3/3	3/3
	3/3	3/3	3/3	3/3	3/3	3/3	3/3	3/3	3/3	3/3
	3/3	3/3	3/3	3/3	2/3	3/3	3/3	3/3	3/3	3/3
	3/3	3/3	3/3	3/3	1/3	3/3	3/3	3/3	1/3	3/3
	3/3	3/3	3/3	3/3	0/3	2/3	3/3	3/3	0/3	3/3
	3/3	3/3	3/3	3/3	3/3	3/3	3/3	3/3	3/3	3/3
	3/3	3/3	3/3	3/3	3/3	3/3	3/3	3/3	3/3	3/3
	3/3	3/3	3/3	3/3	1/3	1/3	1/3	2/3	0/3	1/3
	1/3	1/3	3/3	2/3	0/3	0/3	0/3	0/3	0/3	0/3
	1/3	0/3	3/3	1/3	0/3	0/3	0/3	0/3	0/3	0/3
Water absorption rate (% by weight)	0.53	0.53	0.51	0.51	0.54	0.58	0.58	0.55	0.55	0.54
TMA										
Tg (°C)	195	190	179	191	179	192	194	201	189	192
α (ppm/°C, <Tg)	50	51	53	50	54	53	53	59	57	57
α (ppm/°C, >Tg)	298	291	290	289	379	321	343	302	322	335
Bending modulus (GPa)	19	19	18	19	19	19	19	19	18	19
	12	12	9	12	8	13	14	14	9	13
Room temperature: 25°C										
Breaking strength (MPa)	602	589	579	612	542	502	502	511	532	542
(Yield strength)	(255)	(231)	(200)	(243)	(134)	(245)	(231)	(285)	(188)	(254)
Breaking elongation (%)	3.8	3.7	3.8	3.8	3.4	3.2	3.1	3.2	3.5	3.3
(Yield strength)	(3.9)	(3.7)	(3.8)	(3.8)	(3.3)	(2.3)	(2.3)	(2.2)	(3.5)	(2.5)

[0090]

As can be clearly seen from Table 2, the laminated boards prepared by using varnishes of Examples 1 to 4 are excellent in dielectric characteristics (in particular, dielectric dissipation factor) at room temperature (25°C) and 1 GHz than those of the laminated boards of Comparative examples 1 to 6, in particular, dielectric characteristics of the laminated boards of Examples 3 and 4 in which a monovalent phenol compound was used in combination gave more excellent results. Moreover, dielectric characteristics (in particular, dielectric dissipation factor) of each Example at 90°C are also good, and dependency on temperature change is little. Also, the laminated boards of Examples give better results in solder heat resistance (in particular, at 288°C) under humid conditions as compared to the laminated boards of Comparative examples. Moreover, the laminated boards of Examples give higher values in breaking strength and breaking elongation at room temperature (25°C) and yield elongation at high temperature (200°C) than those of the laminated boards of Comparative examples.

[0091]

[Effects of the invention]

According to the present invention, it could be found that cured products using the resin composition for printed wiring board of the present invention are excellent in dielectric characteristics at high frequency band region, and a drifting property of dielectric characteristics due to change in temperature is also little. Also, they have high bending strength and elongation at glass state region and elongation at high temperatures region. Moreover, the metal clad laminated boards prepared by using the present resin composition for printed wiring board are excellent in humidity and heat resistance under severe conditions using a pressure cooker tester. Accordingly, they can be expected to be members or parts for a printed wiring board

to be used for various kinds of electric and electronic devices which treats high frequency signals of 1 GHz or higher. In particular, the excellent high frequency characteristics and bending characteristics, and high humidity and heat resistance which are characteristics of the resin composition of the present invention are effective for the uses of laminated boards and prepregs to be used for a multi-layered printed wiring board such as a high speed server, router and high speed base station devices, which are required to have heat resistance or crack resistance under severe conditions.

[Document name] Abstract

[Summary]

[Problem] The present invention provides a resin composition for printed wiring board to be used for electronic devices in which operating frequency exceeds 1 GHz, and a varnish, a prepreg and a metal clad laminated board using the same.

[Solving means] A resin composition for printed wiring board characterized in comprising (A) a cyanate ester compound having 2 or more cyanate groups in the molecule and/or a prepolymer thereof, (B) an epoxy resin containing at least one kind of an epoxy resin having a biphenyl structure in the molecule, and a varnish, a prepreg and a metal clad laminated board using the same.

[Selective figure] None